

## REPORT DOCUMENTATION PAGE

Dist: A

Form Approved  
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE  
December 22, 1994

3. REPORT TYPE AND DATES COVERED

Final Report

15 May 92 - 14 Aug 94

4. TITLE AND SUBTITLE

Radiative Lifetime and Quenching Rate Constants of  
PF( $b^1\Sigma^+$ ) and Tests for an Electronic to Vibrational  
Energy Transfer Quenching Mechanism

5. FUNDING NUMBERS

63218C 1601 08

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

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REPORT NUMBER

AFOSR-TR- 95 0044

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/ACRL  
Building 410, Bolling AFB DC  
20332-6448  
Dr. Berman10. SPONSORING/MONITORING  
AGENCY REPORT NUMBER

F49620-92-J-0275

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.

12b. DISTRIBUTION CODE

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13. ABSTRACT (Maximum 200 words)

Methods were developed to generate and isolate the PF( $X^3\Sigma^-$ ,  $a^1\Delta$ ,  $b^1\Sigma^+$ ,  $A^3\Pi$  and  $d^1\Pi$ ) states in a flow reactor. Radiative lifetimes and total removal constants at 300 K have been measured. Except for halogens, the PF( $b^1\Sigma^+$ ) state is stable to chemical reaction. The other PF states seem to participate in chemical reactions at 300 K. Preliminary experiments were done with PCl( $b^1\Sigma^+$ ) and NCl( $b^1\Sigma^+$ ) to establish their radiative lifetimes. The reactions of excess H atoms with PF<sub>2</sub>Cl and PF<sub>2</sub>Br was explored as a chemical source for the generation of PF( $a^1\Delta$ ) from the H + PF<sub>2</sub> secondary reaction.

DTIC QUALITY INSPECTED 3

SUBJECT TERMS PF( $X^3\Sigma^-$ ,  $a^1\Delta$ ,  $b^1\Sigma^+$ ,  $A^3\Pi$ ,  $d^1\Pi$ ) Chemistry, PF(b) Electronic-to-Vibrational, energy transfer, PF(b) lifetime, Quenching Rate Constants (300 k), Gas Phase energy storage

15. NUMBER OF PAGES

12

16. PRICE CODE

17. SECURITY CLASSIFICATION  
OF REPORT

UNCLASSIFIED

18. SECURITY CLASSIFICATION  
OF THIS PAGE

UNCLASSIFIED

19. SECURITY CLASSIFICATION  
OF ABSTRACT

UNCLASSIFIED

20. LIMITATION OF ABSTRACT

19950130 058

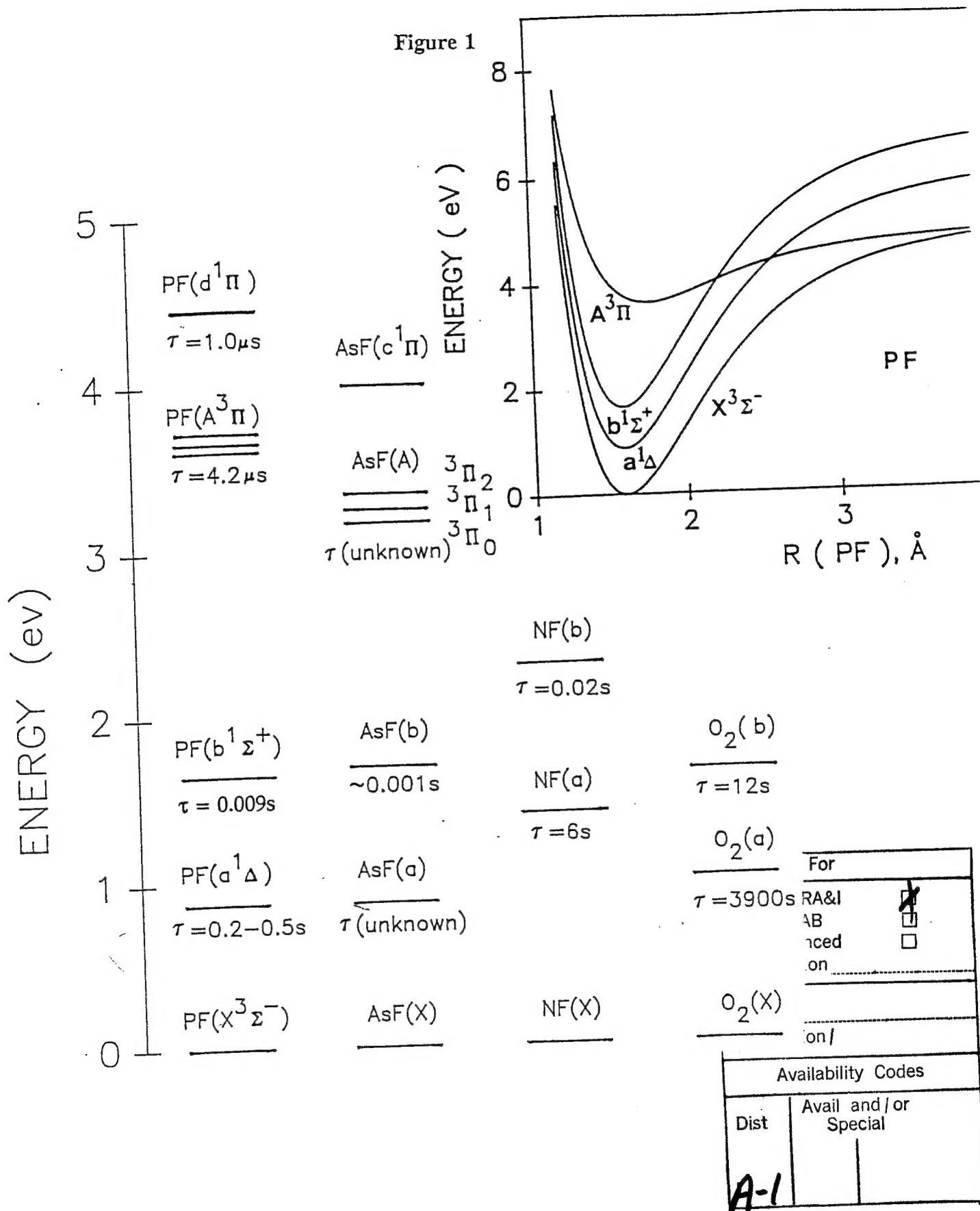
# EXCITED STATE CHEMISTRY OF PF, NF AND NCl

Air Force Office Of Scientific Research (F49620-92-J-0275)

Final Report (May, 1992 - July, 1994)

## A. Introduction

The objective of this research program was to develop the gas phase chemistry for energy storage systems that could serve as the media for short wavelength, electronic-transition lasers. We selected the PF, NCl, and NF molecular systems for study, because of the success in the chemical generation and utilization of the excited singlet states of O<sub>2</sub> in the oxygen-iodine laser. Our primary goals were to develop suitable laboratory sources of the singlet and triplet states of PF (and AsF if time permitted) and to characterize the chemistry of these states. The NF( $b^1\Sigma^+$ ,  $a^1\Delta$  and  $X^3\Sigma^-$ ) states had been studied in a previous AFOSR contract, and some experiments also were done with NCl(b) for comparison with PF(b) and NF(b). Another goal was to develop chemical sources of these molecules that could be scaled to higher concentration and then to utilize this stored energy, perhaps by energy-pooling reactions, to form a suitable upper laser state. All of the Group V diatomic halides molecules have the  $\sigma^2\pi^4\pi^{*2}$  molecular orbital description for the lowest three electronic states, which are the  $X^3\Sigma^-$ ,  $a^1\Delta$  and  $b^1\Sigma^+$  states in order of increasing energy. One attractive feature of PF and AsF and most other Group V diatomic halide molecules (except for NF and NCl) is the existence of a bound  $A^3\Pi_{0,1,2}$  state that, in principle, can serve as an upper laser state. The energies of these states and sketches of the PF(X,a,b,A) molecular potentials are given in Figure 1. If the energy storage properties of the PF singlet states are satisfactory and if energy pooling methods could be developed, then coupling the PF system to a second chemical system to achieve energy extraction (which usually introduces numerous complications) possibly can be avoided. Even if the PF(a) and AsF(a) molecules can not be directly generated by chemical reactions, high concentrations can be



formed by energy transfer from  $O_2(a)$  to their ground states, because of the relative energies of these states. The experiments were done in discharge-flow reactors to isolate suitable concentrations of the individual states, measure rate constants and identify products. Flowing electrical discharge sources were developed for the PF(X, a and b) molecules and for NCl(b). The properties of the PF( $A^3\Pi$  and  $d^1\Pi$ ) states were characterized by laser-induced excitation from PF(X and a). During the two year period, good progress was made in collecting kinetic data for the PF chemical system, but we did not start work with AsF, because the contract was terminated after two years of work.

The research work will be summarized in narrative form in 4 subcategories. The narrative section is followed by a listing of papers published with support of this Air Force contract. The first two papers in the list deal with reactions of NF(a) and NF(X); the laboratory work for those two papers was done with support from an earlier Air Force contract. Other papers describe work related to PF, except one that describes the lifetime and reactions of NCl(b) and PCl(b). For detailed accounts of the work, the reader should consult the published papers.

## **B. Properties of the PF(X,a,A and d) States**

Figure 1 gives a summary of the energies of the PF singlet states, plus the location of the  $A^3\Pi_{0,1,2}$  state. The  $^1\Pi$  and  $^3\Pi$  states arise by promoting an electron from the  $\sigma$  to the  $\pi^*$  antibonding orbital giving the  $\sigma^1\pi^4\pi^{*3}$  configuration. The PCl and AsF systems have energy levels similar to those for PF. The presence of these  $^3\Pi$  and  $^1\Pi$  excited states is what makes LIF such a powerful analytical tool for monitoring the concentration of the three lower states. The radiative lifetimes of the  $^1\Pi$  and  $^3\Pi$  states are  $\sim 1$  and  $4 \mu s$ , respectively, and they have long  $v''$  progressions in their transitions to the lower states. We began our work with the PF system in May of 1992. Progress was rapid because a microwave discharge through dilute flows of He/PF<sub>3</sub> and Ar/PF<sub>3</sub> are rich sources of the PF(X and a) states, as well as PF<sub>2</sub>( $\tilde{B}^2B_2$ ).

Preliminary experiments suggest that electrical discharges through flows of He/PCl<sub>3</sub> also could provide entry into the chemistry of PCl radicals. We were able to generate the PF(X and a) molecules in sufficient concentration to do laser-induced fluorescence, which permitted characterization of the quenching of the PF(A and d) states, as well as the measurement of some reaction rate constants for PF(X and a) with various stable reagent molecules.

A microwave discharge through a dilute PF<sub>3</sub>/He flow provides an excellent source of PF(X<sup>3</sup>Σ<sup>-</sup>) molecules that subsequently can be excited by a pulsed laser to selected vibrational levels of the PF(A<sup>3</sup>Π<sub>0,1,2</sub>) states. Very detailed, state specific relaxation processes of PF(A) can be studied. We completed a comprehensive examination of the electronic state quenching of PF(A, v'=0) by a series of molecular reagents; the vibrational and spin-orbit state relaxation in He and Ar also was studied. These data were acquired by observing the change in the pseudo first-order fluorescence decay constants of PF(A) with added reagent. These data provide the following points of view about the properties of PF(A) as a candidate for an upper laser state.

- (1) The radiative lifetime (4.2 μs) and the long progression in v" is a positive factor.
- (2) The bond energy (≥ 1eV) is adequate to prevent dissociation.
- (3) The stability toward electronic quenching by He and Ar is excellent.
- (4) The vibrational and spin-orbit relaxation rates are fast enough to enable the PF(A, v') populations to reach Boltzmann conditions.
- (5) The quenching rate constants for most molecular reagents, other than perfluorinated molecules, are larger than desirable for applications as a laser.

Identification of the mechanism responsible for the electronic quenching of PF(A) will require measurement of the product state. Based upon the pattern of the quenching constants, we suspect that many of the reagents quench by chemical reaction. However, transfer to a PF\* metastable state is another possibility. No electronic states of PF have been reported that lie near in energy to PF(A); however, molecular orbital considerations suggest that a <sup>3</sup>Δ state could

be in this energy region. An in-depth study of rotational perturbations in the  $\Omega=0,1,2$  states of  $\text{PF}(A^3\Pi_3)$  for a range of  $v'$  levels might provide some evidence about the location of a  $\text{PF}(\Delta)$  state or some other  $\text{PF}^*$  metastable state.

The relaxation mechanism between the three spin-orbit states seems to be complicated with transfer from  $\Omega=2$  to  $\Omega=0$  being faster than transfer  $\Omega=2$  to  $\Omega=1$  in He buffer gas. The relaxation scheme with assignments of the rate constants in He buffer are summarized below. The separation between the spin-orbit levels of  $\text{PF}(\Delta)$  with case a coupling is  $\sim 140 \text{ cm}^{-1}$



The magnitudes of the rate constants for the up-transition are determined by detailed balance. The more facile collisional coupling between  $\Omega=2$  and 0 rather than 2 and 1 or 1 and 0 is in accord with a theoretical prediction. The experimental results in Ar buffer gas differ from He, and the  $\Delta\Omega=\pm 1$  transitions have larger magnitudes than the  $\Delta\Omega=\pm 2$  transitions. The vibrational relaxation rate from  $\text{PF}(A, v'=1)$  is slower than spin-orbit state relaxation, so equilibration within the  $v'=1$  spin-orbit states occurs before the population passes to  $v'=0$ . The magnitudes and pattern for the spin-orbit relaxation rate constants for  $\text{PF}(A^3\Pi_{0,1,2})$  differ from these of the isoelectronic  $\text{SO}(A^3\Pi_{0,1,2})$  case. Very little quantitative data are available in the literature for spin-orbit relaxation processes in  $^3\Pi$  states with case (a) coupling. Comparison of results for the SO, PF, PCl and AsF series of isoelectronic molecules could help elucidate the spin-orbit relaxation and electronic quenching mechanisms for these  $^3\Pi_{0,1,2}$  states, if such experiments were done.

The microwave discharge source for  $\text{PF}(X)$ , i.e., a discharge through a dilute flow of  $\text{PF}_3/\text{He}$ , also provides an adequate concentration of  $\text{PF}(a^1\Delta)$  for excitation to the  $d^1\Pi$  state. We

measured the radiative lifetime for  $\text{PF}(\text{d}^1\text{II})$  as  $0.96\mu\text{s}$ . Quenching constants of  $\text{PF}(\text{d}^1\text{II})$  were measured with several reagents for comparison with the quenching constants of  $\text{PF}(\text{A}^3\text{II})$ . The quenching constants for  $\text{PF}(\text{d})$  are generally larger than for  $\text{PF}(\text{A})$ . The quenching rates constants for  $\text{PF}(\text{d}^1\text{II})$  are very small in He, Ar, and  $\text{CF}_4$ . After characterizing the quenching constants for  $\text{PF}(\text{d})$ , we used the LIF intensity from  $\text{PF}(\text{d} \leftarrow \text{a})$  as a way to measure the relative concentration of  $\text{PF}(\text{a})$  in the flow reactor in the presence of added reagents. These measurements are described in the next paragraph.

After developing the laser-induced method to study the quenching of the  $\text{PF}(\text{A}^3\text{II})$  and  $\text{PF}(\text{d})$  states, we subsequently did a series of experiments to measure the 300 K rate constants for loss of  $[\text{PF}(\text{X})]$  and  $[\text{PF}(\text{a})]$  in the same flow reactor. The experiments were done using the fixed observation point method in the flow reactor with generation of  $\text{PF}(\text{X})$  and  $\text{PF}(\text{b})$  by microwave discharge. The reaction time was  $\sim 5$  ms and the LIF intensities of the  $\text{PF}(\text{A} \leftarrow \text{X})$  and  $\text{PF}(\text{d} \leftarrow \text{a})$  transitions were used to monitor the  $\text{PF}(\text{X})$  and  $\text{PF}(\text{a})$  relative concentrations vs. added reagent concentration. In some cases, correction of the LIF intensities for quenching of the  $\text{PF}(\text{A})$  and  $\text{PF}(\text{d})$  states were necessary. The validity of the method was demonstrated by measuring rate constants for 12 molecular reagents. Except for reactions with  $\text{O}_2$  and  $\text{NO}$ , the  $\text{PF}(\text{a})$  state has larger rate constants than the  $\text{PF}(\text{X})$  state. Just as for  $\text{NF}(\text{a})$ , Lewis base type molecules, such as  $\text{NH}_3$  and  $\text{N}(\text{CH}_3)_3$ , have the largest rate constants for removal of  $\text{PF}(\text{a})$ ; these rate constants were  $\sim 3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . The rate constants for most other reagents reacting with  $\text{PF}(\text{a})$  were less than  $1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . Additional work is needed to obtain a broader characterization of the gas phase chemistry of  $\text{PF}(\text{X}$  and  $\text{a})$ ; the product channels especially need to be identified. The discharge flow-reactor method developed in these experiments is one possible approach to study phosphorous based free radical chemistry, which is largely unexplored.



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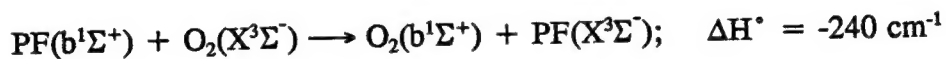
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### C. Characterization of the PF( $b^1\Sigma^+$ ) Reactions

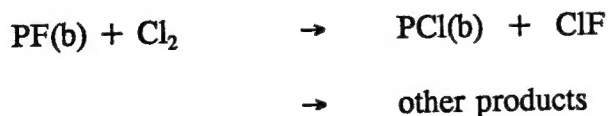
A low power dc discharge ( $\sim 300$  volts) in a dilute mixture of PF<sub>3</sub> in either He or Ar provides an adequate concentration ( $\sim 2.5 \times 10^8$  molecules cm<sup>-3</sup>) of PF(b) to systematically study the quenching rate constants for PF( $b^1\Sigma^+$ ). The relative concentration was monitored by the PF(b-X) transition, which has a radiative lifetime of 9.5 ms. The PF(b) molecules are readily quenched upon contact with the Pyrex glass wall of the reactor, but coating the walls with halocarbon wax provides an inert surface. Gas phase quenching constants at 300K have been measured for 38 reagent molecules. The magnitudes of the rate constants are similar to those for the quenching of NF(b). The rate constants generally are small and the pattern for the magnitudes of the rate constants implies that the mechanism is E-V transfer with concomitant formation of PF(a). The general lack of chemical reactivity of PF(b) (and also PCl(b)) is encouraging with respect to energy storage by singlet PF molecules.

The quenching rate for PF(b) by added O<sub>2</sub> is relatively fast ( $k_{O_2} = 2.1 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>) and from the weak O<sub>2</sub>(b-X) emission we have identified O<sub>2</sub>(b) as a product from the excitation-transfer reaction.



The reaction seems to be quantitative. This reaction can provide O<sub>2</sub>(b) in a flow reactor in the absence of O<sub>2</sub>(a), a rather rare situation.

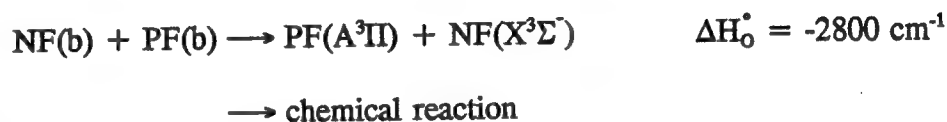
We also have studied the reactive quenching of PF(b) by halogens and NO<sub>2</sub>. These rate constants are 1-2 orders of magnitude larger than for the E-V processes. The reactive quenching by Cl<sub>2</sub> and Br<sub>2</sub> was identified from the formation of PCl(b) or PBr(b), e.g.,



The branching fractions for PCl(b) and PBr(b) formation were estimated as 0.35 and 0.1, respectively. Similar reactions, but with smaller branching fractions, were demonstrated for

NF(b) reacting with Cl<sub>2</sub> and Br<sub>2</sub>. The chemical reactions of the b state molecules with halogens seems relatively general. The mechanism probably is formation of electronically excited intermediate, such as PFCl<sub>2</sub><sup>\*</sup>, molecular state that subsequently eliminates ClF to give PCl(b) or simply dissociates to PFCl + Cl. The reactions with Cl<sub>2</sub> and Br<sub>2</sub> set limits for  $\Delta H_f^\circ(\text{PCl}) - \Delta H_f^\circ(\text{PF}) \leq 17 \text{ kcal mol}^{-1}$  and  $\Delta H_f^\circ(\text{PBr}) - \Delta H_f^\circ(\text{PF}) \leq 26 \text{ kcal mol}^{-1}$ .

The energy-pooling reaction between NF(b) and PF(l(b)) to give PF(A<sup>3</sup>Π) was investigated. The reaction occurs with a very large rate constant, which was estimated as  $\sim 4 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . We have not measured the ratio of the physical energy-pooling rate to the chemical reaction rate.

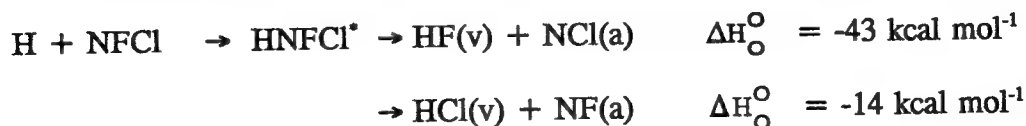


However, the estimated rate constant for energy pooling is so large that physical energy-pooling must be the dominant reaction channel.

During the course of our study of PF(b), we also have discovered and assigned the emission spectrum from the metastable PF<sub>2</sub>( $\tilde{\text{B}}^2\text{B}_2$ ) state. The low power dc discharge in a PF<sub>3</sub>/He flow also generated this long-lived excited state radical. Originally we assigned this long-lived emission spectrum to the ( $\tilde{\text{a}}^4\text{A}_2 - \tilde{\text{X}}^2\text{B}_1$ ) transition. However, recent *ab initio* calculations have shown that the ( $\tilde{\text{B}}^2\text{B}_2 - \tilde{\text{X}}^2\text{B}_1$ ) transition is the preferred assignment.

#### D. Chemical Generation of PF(a)

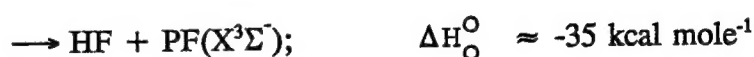
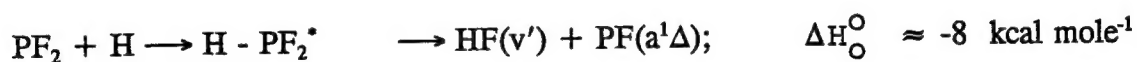
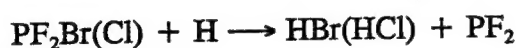
As part of a collaborative effort with Professor Coombe (Denver University), we investigated the reactions of H atoms with NFCl<sub>2</sub>. The main interest was the possibility of a chemical source of NF(a) and HCl(a) from the secondary reaction.



The NFCl reaction does seem to conserve spin and given a<sup>1</sup>Δ state products. Our measurements

were mainly based upon the infrared chemiluminescence from HCl(v) and HF(v). We established a primary rate constant for  $\text{H} + \text{NFCl}_2 \rightarrow \text{HCl} + \text{NFCl}$  as  $1.9 \pm 0.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The combined data from the two laboratories give a branching ratio for  $\text{NCl(a)}/\text{NF(a)} \sim 1/4$  for the secondary reaction, e.g., the reaction favors the least exoergic channel. The  $\text{H} + \text{NFCl}_2$  reaction system can provide a chemical source that generates both  $\text{NCl(a)}$  and  $\text{NF(a)}$ . Additional details about these interesting reactions are provided in the published paper.

We also investigated some similar reactions as possible chemical sources for  $\text{PF(a)}$ . This effort was aided by Mr. C. Liu, a visitor from China. Since the  $\text{H} + \text{PF}_3$  reaction rate is very slow, we investigated  $\text{H} + \text{PF}_2\text{Cl}$  and  $\text{PF}_2\text{Br}$  as a way to produce  $\text{PF}_2$  radicals. The plan was to use the  $\text{H} + \text{PF}_2$  reaction, which by analogy to the  $\text{H} + \text{NF}_2$  and  $\text{NFCl}$  reactions, could conserve spin and generate  $\text{PF(a)}$  with high efficiency. Mr. Liu synthesized the  $\text{PF}_2\text{Cl}$  and  $\text{PF}_2\text{Br}$  samples, since they are not commercially available. The anticipated reaction scheme is given below for excess H atoms.

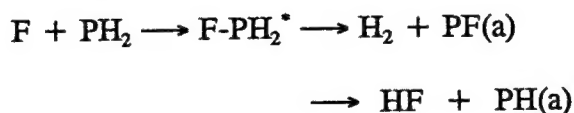


Based upon the observed HF emission intensity and the HF vibrational distribution for short reaction times, the branching fraction for formation of  $\text{PF(a}^1\Delta)$  must be less than 1.0 and the more exoergic triplet channel must have some importance, i.e., spin is not completely conserved. Using the laser-induced technique, both  $\text{PF(X)}$  and  $\text{PF(a)}$  were directly observed from the  $\text{H} + \text{PF}_2\text{Br}$  reaction system with  $\text{PF(d-a)}$  showing the slightly stronger LIF intensity relative to  $\text{PF(A} \leftarrow \text{X)}$ . These results must be combined with the infrared chemiluminescence data from HBr and HF and interpreted. Preliminary interpretations suggest that  $[\text{PF(X)}] < [\text{PF(a)}]$ .

The main experimental difficulty in these experiments was the problem of quantitative gas handling for the  $\text{PF}_2\text{Cl}$  and  $\text{PF}_2\text{Br}$  samples. Although the synthesis is straightforward and the pure sample can be stored at low temperature, unresolved problems with regard to metering the desired pure quantities to the flow reactor from room temperature reservoirs containing mixtures of  $\text{PF}_2\text{Cl}$  or  $\text{PF}_2\text{Br}$  diluted in He or Ar seem to exist. Both molecules seem to react with glass storage reservoirs (stainless steel is worse) and further effort is needed to develop quantitative gas handling techniques for  $\text{PF}_2\text{Cl}$  or  $\text{PF}_2\text{Br}$ . We seem to understand the  $\text{H} + \text{PF}_2$  reaction better than the primary reactions of H atoms with  $\text{PF}_2\text{Cl}$  and  $\text{PF}_2\text{Br}$ .

The  $\text{H} + \text{PF}_2$  reaction differs from the  $\text{H} + \text{NF}_2$  reaction, because the weaker H-P bond and the stronger P-F bond changes the thermochemistry. Thus, formation of  $\text{PF(a)}$  from  $\text{H} + \text{PF}_2$  is only slightly exoergic. Since the  $\text{PF}$  and  $\text{PF}_2$  thermochemistry is not well established, predicting specific products for a given reaction is difficult. Nevertheless, the  $\text{H} + \text{PF}_2$  reaction does have an appreciable branching fraction for generating  $\text{PF(a)}$ , and the analogy to the very useful  $\text{H} + \text{NF}_2$  reaction seems to have some validity.

A second approach to chemically generating  $\text{PF(a)}$  is to use the reaction of excess F atoms with  $\text{PH}_3$ . The first step is known to be direct H abstraction to give  $\text{PH}_2$  and  $\text{HF}$ . In a preliminary experiment, we observed strong  $\text{PF(b-X)}$  emission early in the reaction chain for excess F with  $\text{PH}_3$ . A possible explanation, which remains to be confirmed, is the following two reactions.



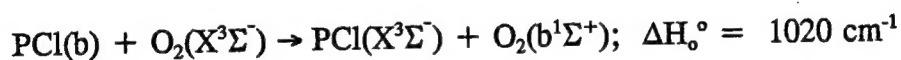
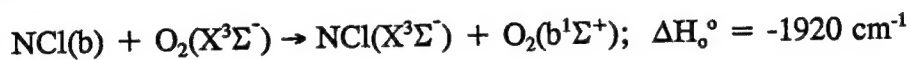
Another possibility is that  $\text{PF(b)}$  was formed in the same step as with  $\text{PF(a)}$ . Further work is needed to characterize the  $\text{F} + \text{PH}_2$  reaction. The next logical experiment is to probe the  $\text{F} + \text{PH}_2$  reaction system by LIF to determine the relative concentration of  $\text{PF(X)}$ ,  $\text{PF(a)}$ ,  $\text{PH(a)}$

and PH(X) and to measure how these concentrations change with time for various [F].

### E. Characterization of NCl( $b^1\Sigma^+$ ) and PCl( $b^1\Sigma^+$ ) Reactions

Passing dilute flows of PCl<sub>3</sub>/He or NFCl<sub>2</sub>/He through the same dc discharge used to generate PF(b) molecules from PF<sub>3</sub> created useful concentrations of PCl(b) and NCl(b). The concentrations of both molecules could be monitored from the b-X emission intensity. Therefore, a series of experiments were done to obtain the two radiative lifetimes and a general pattern for the quenching constants of NCl(b). Less work was done for PCl(b), but the method was demonstrated. The radiative lifetimes of NCl(b) and PCl(b) are  $2.4 \pm 0.4$  and  $4.5 \pm 2.0$  ms, respectively, which are the best values in the literature. The magnitude of the quenching rate constants for most molecular reagents at 300 K are in the range of  $10^{-13}$  -  $10^{-14}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> except for halogens. The molecular halogens quench by chemical reaction, whereas most other molecules quench by a physical E→V transfer mechanism. The pattern for the magnitudes of the quenching rate constants vs. reagent are similar to those for PF(b).

Experiments were done with O<sub>2</sub> to obtain the rate constants for the excitation-transfer reactions.



The 300 K rate constants are  $1.0 \times 10^{-12}$  and  $< 1 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, which are consistent with the  $\Delta H_0^\circ$  values for energy transfer. The slow reaction rate of PCl(b) with O<sub>2</sub> implies that chemical interaction does not occur. This is contrary to the results for PF(a) and PF(X) reacting with O<sub>2</sub>, which have large rate constants.

The flow reactor with the weak dc discharge method developed in this work to generate singlet  $b^1\Sigma^+$  state molecules could be used to further characterize the properties of PCl(b), PBr(b) and probably AsF(b).

## CUMULATIVE LISTING OF PUBLICATIONS

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5. E. Arunan, C.P. Liu, D.W. Setser, J.V. Gilbert and R.D. Coombe, "Infrared Chemiluminescence Studies of the H + NFCl<sub>2</sub> and H + NFCl Reactions", J. Phys. Chem., 98, 494 (1994).
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